SYNTHESIS OF MESOPOROUS CARBONS THROUGH INVERSE REPLICATION AND SELF-ASSEMBLY

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Abstract

Mesoporous carbons have recently attracted much attention, because of their usefulness as adsorbents for large molecules, components of electrochemical double-layer capacitors, catalyst supports and so forth. One of important recent achievements in this field was the synthesis of ordered mesoporous carbons through inverse replication of ordered mesoporous silica templates [1]. Herein we describe the combination of this approach with another novel route to nanostructured carbons based on the pyrolysis of nanoscale phase-separated block copolymers [2]. In the latter route, one block, e.g., polyacrylonitrile (PAN), serves as carbon precursor whereas the other block, immiscible with the first one, induces self-assembly into a variety of nanostructures and is sacrificed upon pyrolysis. Use of an organic sacrificial block, which is volatilized before carbonization of the carbon precursor block, poses the challenge in replicating and preserving of bulk nanostructure, in particular in maintaining the connectivity of mesopores. We have now designed a new system, in which sacrificial block is water soluble and is used as a template for formation of silica. Silicious phase acts as a scaffolding supporting the evolving carbon phase during the pyrolysis and is subsequently etched away, leaving behind mesoporous carbon. Appropriate copolymers were synthesized using atom transfer radical polymerization (ATRP) which provides necessary control over the polymer composition and molecular weight. Mesoporous carbons obtained from these novel precursors exhibited high specific surface area (typically 750-1000 $m^2 g^{-1}$), large pore volumes (up to 2.8 $cm^3 g^{-1}$) and pore diameters ranging from about 4 to 25 nm. In contrast with most mesoporous carbons reported to date, they exhibited very low microporosity. We also explored the synthesis of ordered nanoporous carbons from PAN via the inverse replication procedure [3]. The polymerization of acrylonitrile in the pores of ordered mesoporous silica templates was performed, followed by PAN stabilization and carbonization, and by the dissolution of the silica template. The obtained ordered mesoporous carbons exhibited high specific surface areas (700-1000 $m^2 g^{-1}$) and large pore volumes (0.8-1.8 $cm^3 g^{-1}$). The templates, precursors and carbons were extensively characterized using nitrogen adsorption, thermogravimetry, transmission electron microscopy, Raman spectroscopy and powder X-ray diffraction.

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